

APPENDIX 1

Handbook of
**SPECIALTY
ELASTOMERS**

Edited by
Robert C. Klingender



heat resistance of CSM coupled with better low-temperature properties. The dynamic properties are also much better than CSM, which are essential for this application. More detail is given in the ACSM section of this chapter. The compound should use modulus to large size black fillers, no plasticizer and a cure system to provide a high modulus and a low tan delta such as tillarge 20 phr, magnesia 10 phr, Tetrone A 2 phr, MBTS 0.5 phr, and NIBC 3 phr.

ACKNOWLEDGMENT

I thank DuPont Specialty Elastomers L.L.C. for supplying the technical information upon which this chapter is based and for the able assistance of Charles R. Baldorf.

REFERENCES

1. Maurice Morton (ed.), *Rubber Technology*, Third Edition, Chapter 12, Part II, Van Nostrand Reinhold, New York, 1987, 638 pp.
2. Charles R. Baldorf, Hyposal® Chlorosulfonated Polyethylene and Acsum®, Alkylated Chlorosulfonated Polyethylene lecture presented to The Chicago Rubber Group, Inc. February, 2003.
3. DuPont Hyposal® Technical Information HPE-H68577-00-C1070, "Types, Properties and Uses of Hyposal," Rev. 3 November, 2002.
4. TOSOH Synthetic Rubber Bulletin, cation, TOSQ-CSM and SKYPRENE.
5. DuPont Hyposal® Technical Information HPE-H68570-00-B0401, "Selecting a Filler," Rev. 3 November, 2002.
6. DuPont Hyposal® Technical Information HPE-H73616-00-C1102, "Selecting a Plasticizer and Processing Aid," Rev. 2 January, 2001.
7. DuPont Hyposal® Technical Information HPE-H68574-00-C1102, "Selecting a Curing System," Rev. 2 November, 2002.
8. DuPont Hyposal® Technical Information HPE-H73616-00-C1103, "Compounding Hyposal for Wear Resistance," Rev. 2 November, 2002.
9. DuPont Hyposal® Technical Information HPE-H68574-00-C1102, "Processing Hyposal," Rev. 2 November, 2002.
10. DuPont Acsum® Technical Information H-79944, "Product and Properties Guide," June, 1998.

10 Ethylene Vinyl Acetate Elastomers (EVM) (ASTM Designation AEM)

Hermann Meisenheimer and Andrea Zens

CONTENTS

10.1	Introduction.....	344
10.2	Polymerization and Production Process.....	344
10.3	Structure Property Relationships.....	346
10.3.1	Classification and Commercial Products.....	346
10.3.2	Thermal Stability and Heat Aging Properties.....	347
10.3.3	Glass Transition Temperature and Crystallinity.....	348
10.3.4	Oil Resistance.....	354
10.4	Compounding.....	355
10.4.1	Curing System.....	355
10.4.2	Antioxidants.....	356
10.4.3	Fillers.....	356
10.4.4	Plasticizers.....	357
10.4.5	Miscellaneous.....	357
10.5	Processing.....	357
10.5.1	Mixing.....	357
10.5.2	Extrusion.....	357
10.5.3	Calendering.....	357
10.5.4	Fabricating.....	357
10.5.5	Molding.....	358
10.5.6	Steam Curing.....	358
10.5.7	LCM Salt Bath Curing.....	358
10.6	Applications.....	358
10.6.1	High-Temperature Insulation Compounds.....	358
10.6.1.1	Maximum Service Temperature.....	358
10.6.1.2	Resistance to Ultraviolet Light, Weathering, and Ozone.....	359
10.6.1.3	Radiation Resistance.....	360
10.6.1.4	Electrical Properties.....	361

10.6.2	EVM for Flame-Retardant Noncorrosive Applications.....	361
10.6.2.1	Influence of Amount of Filler.....	362
10.6.2.2	Toxicity, Smoke Density, and Corrosivity of Combustion Gases.....	363
10.6.2.3	Influence of Vinyl Acetate Content on Oil Swelling.....	363
10.6.3	Heat- and Oil-Resistant Molded Goods.....	364
10.6.4	EVM as a Blend Component.....	366
10.6.5	Outlook for New Applications.....	367
	References.....	368

10.1 INTRODUCTION

Ethylene vinyl acetate elastomers belong to the class of specialty rubbers. The first patents on this copolymer were granted to ICI in 1938 [1]. But it took over 20 years until the polymerization process was optimized and the first products were commercially available [2]. Today, a variety of copolymers spanning a wide range of vinyl acetate contents are on the market as given in Table 10.1.

This chapter first discusses the polymerization conditions and production processes. An overview of the raw material properties and the influence of the comonomers ratio on the copolymer will follow. Some applications, compounding, and processing suggestions will be discussed in the last part.

10.2 POLYMERIZATION AND PRODUCTION PROCESS

The polymerization reaction is shown in Figure 10.1.

TABLE 10.1
EVM Commercial Products

VA-Content %	Trade Name	Company
28	Elasto 250	Dupont
	Elasto 260/285	Dupont
40	Levaflex 400	Bayer
	Elasto 408.05/408.18	Dupont
	Elasto 40 W	Dupont
	Ecolux 40	Mitsui-Dupont
45	Levaflex 450/450 HV	Bayer
	Elasto 46.1	Dupont
	Ecolux 45	Mitsui-Dupont
50	Levaflex 500 HV	Bayer
60	Levaflex 600 HV	Bayer



FIGURE 10.1 Polymerization reaction for EVM.

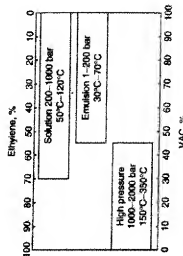
Ethylene and vinyl acetate are copolymerized to a poly (ethylene-co-vinyl acetate). The reaction can be carried out in every ratio of the comonomers as the reactivity ratios are close to 1 [3,4]. Consequently, the distribution of the comonomers along the chain is random.

The versatility of the copolymer class is established by these copolymerization parameters. The mechanism of the reaction is a radical chain copolymerization, initiated by, for example, *azo* compounds.

Vinyl acetate acts as a chain-transfer agent giving rise to a broad molecular weight distribution and, in the case of a bulk polymerization, a limited molecular weight. This problem can be overcome by polymerizing in solution, for example, in toluene, benzene, heptane, or tertiary butanol [5].

Tertiary butanol is preferred because of its low chain-terminating properties. Three different methods for the production of ethylene vinyl acetate copolymers are known, these being: high-pressure process (0%–45% vinyl acetate); low-pressure emulsion process (55%–100% vinyl acetate); and medium-pressure process in solution (30%–100% vinyl acetate).

Figure 10.2 gives an overview of the production conditions and the vinyl acetate range covered.



The high-pressure process was developed from the high-pressure polyethylene process (LDPE). The polymerization is carried out in bulk. By means of this process mainly copolymers with a vinyl acetate content of up to 45% are produced. The important range lies between 5% and 30% vinyl acetate content, giving copolymers with thermoplastic properties. The maximum molecular weight achieved by the high-pressure process is comparatively low due to the high chain-transfer activity of the vinyl acetate in bulk polymerization. Therefore, the vinyl acetate content is limited.

The emulsion process yields material with vinyl acetate content between 45% and 100%. Emulsion-polymerized material is rarely used in the rubber industry, but rather in thermoplastic applications as an impact modifier.

The solution process is carried out in tertiary-butanol solution under medium pressures [6]. The maximum molecular weight reached is higher than that of the high-pressure process because the chain-transfer activity of the vinyl acetate monomer is reduced in solution. A more detailed description of the different processes is given by Gilby [2].

The main feature of poly(ethylene co-vinyl acetate) is the fully saturated backbone, which leads to some outstanding properties such as good resistance against heat, weathering, and ozone and, depending on the vinyl acetate content, oil. These elastomers also have excellent color stability, low compression set, and high capacity for filler loading and good processability. Since the polymers are halogen free, they are used for low smoke insulation and sheathing and can be compounded for excellent flame resistance.

10.3 STRUCTURE PROPERTY RELATIONSHIPS

10.3.1 CLASSIFICATION AND COMMERCIAL PRODUCTS

As already mentioned, ethylene vinyl acetate copolymers can be synthesized in every ratio of the comonomers. The resulting polymers exhibit the complete scale of properties from thermoplastic material to elastomers. Polyethylene is a well-known thermoplastic with a very low glass transition temperature at about -120°C and very high crystallinity of 40%–60%. Polyvinyl acetate is also a thermoplastic, but with a glass transition temperature of 28°C and completely amorphous structure.

If one adds vinyl acetate to the polyethylene chain, for example, up to about 33% by weight, the copolymers are still thermoplastic. Elastomers result by copolymerizing at least 40% by weight vinyl acetate [7].

As shown in Figure 10.3, the "rubber region" reaches up to 80% vinyl acetate. Above this point, the properties of the poly(vinyl acetate) become predominant.

As a result of the different properties of the material, the rubber copolymers are indicated here as "EVM," according to the rubber nomenclature, with the "M" standing for the saturated backbone. We prefer the abbreviation "EVM" instead of "EAM," as prescribed in ASTM D 1418-85, to avoid confusion with ethylene-acrylate copolymers, coded as AEM. The thermoplastic material is denoted by

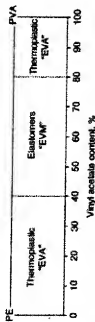


FIGURE 10.3 EVM content produces either elastic or plastic polymers

A survey of the EVM grades available on the market is presented in the following. Table 10.2 shows the different EVM grades from Bayer AG (Germany), which are known as "Levapren."

They differ in vinyl acetate content and Mooney viscosity or melt flow index (MFI).

The chart in Table 10.1 gives an outline of the major EVM elastomers on the market with respect to vinyl acetate content without laying claims to completeness.

The following discussion will primarily deal with copolymers of the 40–80 wt% vinyl acetate range, because they are the most interesting for the elastomer sector. Data for the thermoplastic ethylene vinyl acetate copolymers will be given as necessary for comparison with the elastomers.

10.3.2 THERMAL STABILITY AND HEAT AGING PROPERTIES

Thermo gravimetric measurements can give some information about the heat aging properties and the decomposition behavior of a polymer. Figure 10.4 shows typical

TABLE 10.2
Grades of Levapren EVM from Bayer

Trade Name	Weight% VAC	Viscosity ME (1 + 4) 100°C	Viscosity MFI (g/10 min)
Levapren 400	40 ± 1.5	20 ± 4	≤5
Levapren 450	45 ± 1.5	20 ± 4	≤5
Levapren 500 IV	50 ± 1.5	27 ± 4	≤5
Levapren 600 IV	60 ± 1.5	27 ± 4	≤5
Levapren 700 IV	70 ± 1.5	27 ± 4	≤6
Levapren 800 IV	80 ± 2.0	28 ± 6	≤6
Levapren VP KA 6784	70 ± 1.5	n/60	n/60
Levapren VP KA 8815	60 ± 1.5	n/55	n/55
Levapren VP KA 8857	50 ± 1.5	n/55	n/55
Levapren VP KA 8916	40 ± 1.5	n/55	n/55
Levapren VP KA 9939	91 ± 2.0	n/38	n/38

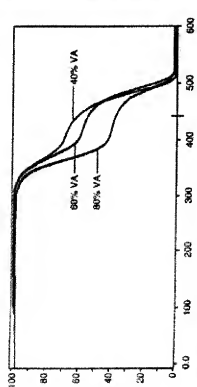


FIGURE 10.4 Thermo gravimetric measurements of 40, 60, and 80 wt% EVM copolymers. Heating rate 20°C/min.

thermo gravimetric measurements in a nitrogen atmosphere. The dynamic measurement was carried out with samples of 40, 60, and 80 wt% vinyl acetate. The decomposition of the copolymer occurs in two steps: the first varying with the level of vinyl acetate content of the sample; the higher the vinyl acetate content, the more pronounced is the first step. The initiation temperature of about 330°C is the same for all copolymers. This leads to the conclusion, that the first step is related to the cleavage of acetic acid from the copolymer. A plot of the height of the first step as a function of the vinyl acetate content, Figure 10.5 indicates a linear relationship, which reinforces the assumption.

The second step is attributed to the decomposition of the polymer backbone. In air the same two-step mechanism is found, but the initiation temperature of the first step drops to 280°C–300°C. The heat of combustion (ΔH_c) of EVM polymers is given in Table 10.3.

The similarity of all copolymers as far as the heat-aging properties are concerned can also be demonstrated by investigating the heat aging of a compound.

A black-filled standard compound was aged for 14 days at 150°C. Figure 10.6 shows the test results, in terms of the tensile strength. Figure 10.7 shows elongation at break, and Figure 10.8 hardness. The results obtained after aging of the samples show a good retention of the properties.

10.3.3 GLASS TRANSITION TEMPERATURE AND CRYSTALLINITY

Both properties are very important for the cold flexibility of an elastomer. Polyethylene exhibits very high crystallinity, because of the regular structure of the polymer chain. Vinyl acetate molecules with their bulky acetate side-chains disturb the regularity and consequently reduce the crystallinity.

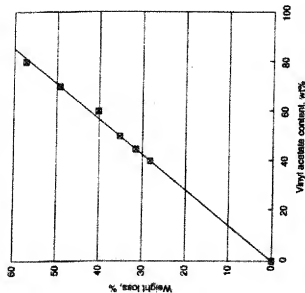


FIGURE 10.5 Weight losses during initial decomposition versus vinyl acetate content.

is measured in the same run. Two typical DSC-curves for a 40 and 60 wt% vinyl acetate copolymer are plotted in Figure 10.9.

The broad melting transition of the 40% EVM is found at -20°C to $+60^\circ\text{C}$ with a maximum at 35°C indicating a poor crystalline order. The thermogram of the 60 wt% EVM copolymer in Figure 10.10 exhibits only a glass transition.

The crystallinity can be calculated from the heat of fusion by dividing it by the value known for ideal crystallized polyethylene which is 293 J/g. The data of

TABLE 10.3
Heat of Combustion (ΔH_c)
of EVM Elastomers

Vinyl Acetate Content (wt%)	ΔH_c (MJ/kg)
40	36.7
45	35.9
50	34.4
60	32.0
70	29.1

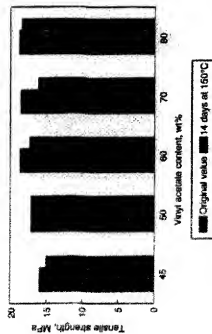


FIGURE 10.6 Original and aged tensile strength versus vinyl acetate content (Aged 14 days at 150°C in air)

the heat of fusion, melt transition, and crystallinity are listed in Table 10.4, together with the glass transition temperatures.

Melting endotherms are only found in samples with vinyl acetate contents up to 50 wt%. Copolymers with higher vinyl acetate content do not have the ability to crystallize because of the interruption of the regular chain structure. In Figure 10.11, the dependence of the heat of fusion on the vinyl acetate content is depicted. As the vinyl acetate content increases the heat of fusion decreases. As a result, the crystallinity shows the same trend, as seen in Figure 10.12.

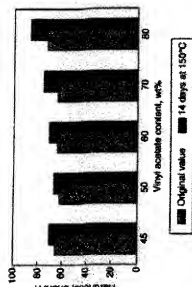
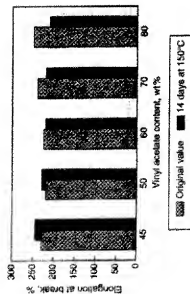


FIGURE 10.8 Original and aged hardness versus vinyl acetate content (Aged 14 days at 150°C in air)

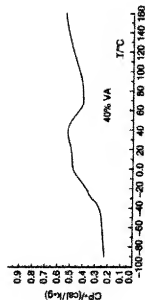


FIGURE 10.9 DSC Scan of 40 wt% vinyl acetate copolymer.

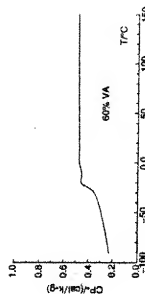


TABLE 10.4
Heat of Fusion (ΔH_f), Crystallinity, Maximum Melt
Temperature (T_m), and Glass Transition Temperature (T_g) of
Various Ethylene Vinyl Acetate Copolymers, HDPE and PVAC

Wt% Vinyl Acetate	T_m (°C)	ΔH_f (J/g)	Crystallinity	T_g (°C)
0 (HDPE)	133	293	—	-120
17	91	92	31	-35
22	86	75	26	-35
27	77	65	22	-34
40	36	36	12	-33
45	25	27	9	-32
50	12	17	6	-31
70	—	—	—	-25
80	—	—	—	-9
100 (PVAC)	—	—	—	-4
				28

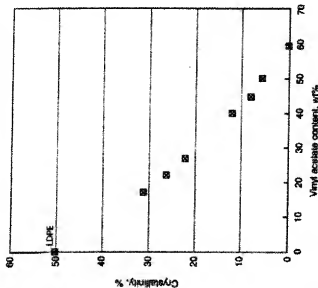
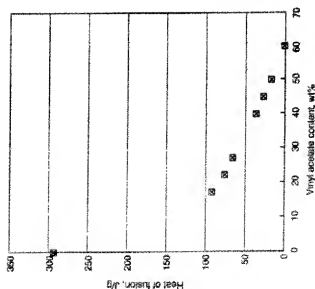


FIGURE 10.12 EVM Crystallinity versus vinyl acetate content.

The maximum temperature of the melting peaks decreases with increasing vinyl acetate content. This is due to a deterioration of the crystallite's perfection. The ethylene sequences, which are able to crystallize, become smaller and, thus, the resulting crystallites are smaller and less perfect. The biggest part of the melting endotherm of the 50 wt% EVM is found below room temperature. Therefore the contribution of crystallites to the tensile strength at room temperature is negligible. In the case of the 40 wt% EVM nearly 50 of the crystallites are already molten at room temperature.

The plot of the glass transition temperature versus the vinyl acetate content is shown in Figure 10.13.

Here the values are nearly constant up to an amount of 50 wt% vinyl acetate. Then the glass transition temperature increases steadily. By extrapolation of the data to the value of polyvinyl acetate, the measured value is found.

Further studies carried out on an aluminum-triethylene filled FRNC compound (compounding see Section 6.2) showed similar results. In Figure 10.14 the results of a torsion pendulum measurement are shown. The values of the first maximum are approximately equal to the 40, 45, and 50 wt% copolymer-based compound, whereas the higher vinyl acetate content leads to increasing maxima.

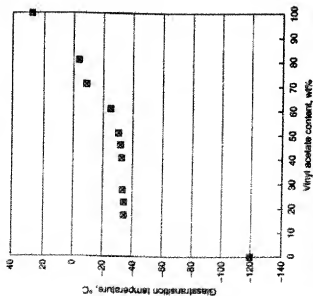


FIGURE 10.13 Glass transition temperature versus vinyl acetate content. (DSC measurements, heating rate 20°C/min.)

10.3.4 Oil Resistance

Oil resistance is closely related to the polarity of an elastomer. The polarity of EVM elastomers is determined by the vinyl acetate content because of the polar nature

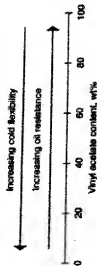


FIGURE 10.15 Relationship of cold and oil resistance with VA content.

of this comonomer. This behavior is monitored by studying the resistance of an FRNC compound to ASTM Oil No. 3. The results of the investigation are shown in Section 6.2.3.

The measurements confirm the assumption derived from the chemical structure of the copolymer. Good oil resistance is found for the high vinyl acetate content copolymers, whereas those with lower vinyl acetate content show poorer oil resistance, as schematically shown in Figure 10.15.

To summarize, EVM vulcanizates possess an excellent heat aging resistance but there is an inverse relationship between best cold flexibility and best oil resistance. The cold flexibility increases with decreasing vinyl acetate content and the oil resistance decreases. So it is up to the compounder to choose the appropriate copolymer in order to meet the requirements of the finished product.

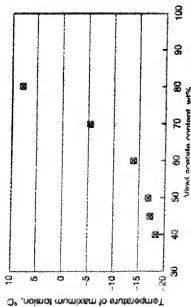
10.4 COMPOUNDING

10.4.1 CURING SYSTEM

EVM elastomers belong to the group of rubbers with fully saturated backbone. As there are no sulfur-curable sites in the side-chain, they have to be cured radically by means of peroxides or high-energy radiation.

The mechanism of the reaction is first an abstraction of a hydrogen atom from the polymer chain, leading to the formation of a reactive radical site [6]. Then two polymer radicals can combine, which results in a polymer network. The network formed by those reactions is very irregular. In order to improve the network the addition of compounds with multiple double bonds, for example, triallyl cyanurate (TAC), triallyl isocyanurate (TACI), trimethylol propane trimethacrylate (TMPTA), or ethylene dimethacrylate (EDMA) is necessary [6]. They are often referred to as activators. The effect is described as an addition to the radical site at the polymer chain and transfer of the radical to the activator. The network is formed by reaction of the transferred radical with another chain.

The selection of the appropriate peroxide is determined by the mixing temperature and the possible need for odorless articles. Among the peroxides available on the market 1,4-bis(t-butyl peroxy isooctoyl) benzene has found widespread



dicumyl peroxide is often used for curing at lower temperatures (150°C–160°C). The quantities recommended for typical light-colored compounds are 2–7 phr of peroxide (absorbed 40% on inactive fillers). The recommended amount of activator is 0.5–5 phr. Carbon black filled compounds may require 25% less peroxide.

Although zinc oxide is not necessary with peroxide cures, it does slightly improve aging properties.

10.4.2 ANTIOXIDANTS

Having no reactive double bonds EVM elastomers have an inherently excellent heat resistance. But for an optimum stability it is necessary to add approximately 1 phr of an antioxidant. Here it is necessary to select the right substance, because many well-known antioxidants cannot be used in peroxide cure. For an optimum heat resistance, the addition of 1 phr of styrenated or octylated diphenylamine (SDPA or ODPA) is recommended. Arylated phenols can be used as nonstaining antioxidants. To protect the vulcanizates from hydrolysis at elevated temperatures and higher humidity, the addition of a polycarbodiimide may be necessary.

10.4.3 FILLERS

The most suitable carbon blacks and typical ranges used are N 330, N 550 (up to 60 phr), N 770 (up to 80 phr), and N 990 (up to 100 phr). N 220 can be used in a blend with other carbon blacks. Conductive compounds often use N 472 carbon black.

White fillers have to be selected more carefully because they can affect the degree of vulcanization. Good results have been achieved by using talcum (micropulverized), neutral clay (50–100 phr), and silica (up to 60 phr). Active silica provides higher tensile strengths but the degree of curing is reduced. A vinyl silane is recommended with white fillers.

For flame-resistant vulcanizates the use of 100–200 phr aluminum trihydrate with a vinyl silane is recommended along with zinc borate at the 10–20 phr level and 0–20 phr of magnesium carbonate. Details of compounding principles will be discussed later.

10.4.4 PLASTICIZERS

The use of plasticizers is not mandatory in EVM grades with low Mooney viscosity. Plasticizers can be used especially in compounds based on high viscosity grades, or in highly filled mixtures.

The most appropriate extenders for EVM mixes are paraffinic mineral oils. Naphthalene and aromatic oils are not recommended because they can affect the peroxide cure.

Synthetic plasticizers should be added to improve the cold flexibility of high vinyl acetate containing grades. Good results have been obtained by using sebacic.

10.4.5 MISCELLANEOUS

Stearic acid (1 phr) is frequently used to reduce sticking of mixes based on low-viscosity EVM. The dispersion of fillers is improved at the same time. Zinc stearate at 1–2 phr is also an alternative.

Panifin wax is not required as an ozone protector but 5 phr is very helpful as a processing aid.

Coloring agents should be selected carefully as many organic pigments disturb the peroxide cure. Acid-free inorganic pigments are therefore recommended.

Unstained, low-pH, and sulfur-bearing materials such as resins, acidic light-colored fillers, and vulcanized vegetable oils should be avoided because of the presence of peroxides.

10.5 PROCESSING

10.5.1 MIXING

Normal methods of mixing may be employed with EVM such as either upside down or conventional mixing in an internal mixer. EVM with low viscosity bands quickly on a mill, whereas higher-viscosity grades may require a breakdown period to achieve a smooth band. Release agents such as stearic acid or zinc stearate should be added with the polymer to reduce mill sticking. Other release agents are vinyl silane, paraffin wax, or commercial internal lubricants.

Fillers should be added early without plasticizer for effective dispersion. The peroxide and cures are best incorporated at the end of the mix.

Care should be taken to ensure that the equipment is clean to prevent contamination that will react with the peroxide curative.

10.5.2 EXTRUSION

Higher-filler loadings are advantageous to stiffen the low-viscosity EVM polymer. Higher-viscosity grades of EVM should be used if possible. If curing in open steam, add 3–5 phr of a polycarbodiimide, such as Rheogran P 50.

10.5.3 CALENDERING

As with extruding of EVM, a high compound viscosity through the use of higher-viscosity elastomers and higher-filler loadings is best. Increased amounts of stearic acid or zinc stearate are also recommended. Roll temperatures of 70°C are suggested.

10.5.4 FABRICATING

EVM has poorer tack at low temperatures, hence the components are best if prewarmed. Low-viscosity elastomers and the use of higher levels of plasticizer

10.5.5 MOLDING

Since EVM must be cured with peroxide, injection or transfer molding works well as air is excluded to a large extent. Mold design is important for intricate shapes since EVM has poor hot tear properties and demolding can be difficult.

10.5.6 STEAM CURING

As with any peroxide-cured compound, it is important to vent all the air from the autoclave to prevent a sticky surface on the vulcanizate. CV steam tube cures generally work well.

10.5.7 LCM SALT BATH CURING

EVM can be cured very effectively at 200°C to 240°C using this method as long as the extrusion is kept under the surface of the salt bath or a salt spray is used to exclude any air.

10.6 APPLICATIONS

The following sections will identify some applications in which EVM is especially advantageous.

10.6.1 HIGH-TEMPERATURE INSULATION COMPOUNDS

This part presents the results of tests made with an insulation compound. Table 10.5 shows the formulation of a typical compound. EVM is used as an insulation material for special electrical conductors that have to withstand service temperatures up to 120°C. The required properties have been specified in VDE 0207/part 20 type 401.

10.6.1.1 Maximum Service Temperature

On the assumption that the elongation at break of an EVM vulcanizate changes at a constant rate in the course of aging, the maximum service temperature was

TABLE 10.5

Insulation Compound

EVM (40% VA)	100.0	Levapren 400, Bayer
Polyethylenedimethylsiloxane	8.0	Rhomogran P 50, Rhain Chemie
Antioxidant SDA	1.0	Vulkoxol DDA, Bayer
Zinc stearate	2.0	
Micro talc	80.0	Minoc Vapor, Lucanex America
Paraffin wax (55°C)	5.0	
Peroxide	6.0	Perkadox 14/60, AKZO

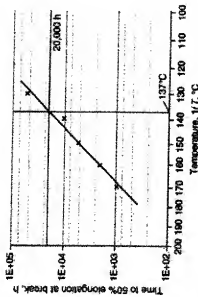


FIGURE 10.16 Arrhenius plot of EVM insulation compound (IEC 216).

determined according to IEC 216, taking the residual elongation at break as the relevant criterion. For each of the aging temperatures between 130°C to 170°C the time that elapsed until the elongation at break fell to 50% was plotted in hours (in logarithmic scale) versus the reciprocal test temperature (in K^{-1}). A straight line is formed (the Arrhenius plot), representing the service life of the insulation compound at the respective temperatures.

The point at which the straight line intersects the time limit (20,000 h) specified in IEC 216 gives a maximum service temperature of 137°C for this vulcanized EVM insulation compound, as shown in Figure 10.16.

10.6.1.2 Resistance to Ultraviolet Light, Weathering, and Ozone

Table 10.6 shows the changes in mechanical properties after UV exposure and weathering. Samples have been irradiated with an ultraviolet lamp of 300 W and 700 Lux.

Specimens exposed outdoor for 10 months at the Levenhues-Engelfeld testing station, a nonindustrial area, showed minor changes in properties. No crazing was detected even after 2.5 years, as given in Table 10.6.

TABLE 10.6

Weathering Effects on EVM Properties UV Light 300 W, 700 Lux

Weathering 10 Months	Ultraviolet Light 7 Days at 47°C
Tensile strength, change %	-12
	+3

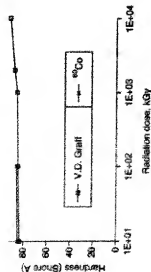


FIGURE 10.17 Effect of radiation on hardness of EVM compound. (Van de Graff accelerator to 100 kGy with a ^{60}Co source at room temperature and 65% relative humidity.)

In an ozone test, specimens were exposed at an elongation of 60% to a concentration of 250 ppm ozone at temperatures of 20°C and 50°C. No crack formation was observed during an exposure time of 14 days.

10.6.1.3 Radiation Resistance

Samples were exposed to two different sources of radiation:

1. A Van de Graff accelerator, current 10^{-4} A, voltage 1.5 MeV at 200 W; test at room temperature and a relative humidity of 65%; radiation rate 900 kGy/h.
2. A 5.55 TBq ^{60}Co source for irradiation at a rate of 9.2 Gy/h; test at room temperature and a relative humidity of 65%.

In Figures 10.17 and 10.18 the mechanical property data measured in the experiments are plotted versus the radiation dose. The influence of the difference in radiation is nearly equal.

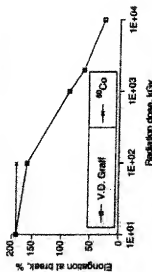
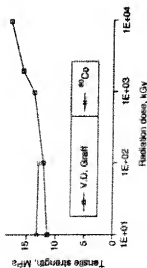


FIGURE 10.19 Effect of radiation on EVM compound. (Van de Graff accelerator to 100 kGy with a ^{60}Co source at room temperature and 65% relative humidity.)

Assuming a residual elongation of 50% as the lowest acceptable value, the EVM vulcanizates can be said to have a radiation resistance of 400 Mrad, as shown in Figure 10.19.

10.6.1.4 Electrical Properties

The electrical properties of the insulation compound were determined on 1 mm thick sheets that had been vulcanized in a press for 20 min at 160°C. The results are shown in Table 10.7.

10.6.2 EVM FOR FLAME-RETARDANT NONCORROSIVE APPLICATIONS

For certain safety reasons some rubber articles must meet stringent requirements, such as

1. Flame retardance
2. Low smoke formation
3. Noncorrosive combustion gases
4. Low toxicity of combustion gases

Table 10.8 shows the formulation of a typical flame-retardant noncorrosive (FRNC) compound.

The favorable performance of such a compound in case of fire is shown in Section 10.6.2.2. For mechanical and thermal properties see Section 10.3.2.

TABLE 10.7

Electrical Properties of an EVM Insulation Compound

Volume resistivity ρ_v	$5 \cdot 10^9$ ($\Omega \cdot \text{cm}$)	VDE 0303/Part 3, IEC 93
Dielectric constant ϵ_r	3.9	VDE 0303/Part 2

TABLE 10.8

Flame-Resistant Noncorrosive Compound (FRNC)

EVM	100.0	Lexipren, Borel
Polycarbonitrile, catalyzed	3.0	Resomgran P 50, Rhon Chemie
ATH Aluminum trihydrate	190.0	Alphat B 126, Bayer
Silica	2.0	RC 1, Union Carbide
Zinc borate	10.0	
Anticorrosion SDVA	1.0	Vulkumol DDA, Bayer
Diethyl sebacate	6.0	
Trimethylolpropane trimethacrylate	0.5	
Potassium	6.0	Perkadox 14/40, AKZO
Total	318.5	

10.6.2.1 Influence of Amount of Filler

In the case of polymers that are not "intrinsically flame retardant," good flame-retardant behavior is only possible if the compound is heavily loaded with flame-retardant fillers. The filler most widely used is aluminum trihydrate (ATH). Figure 10.20 shows the combustion behavior of a sample according to the limiting oxygen index (LOI) and critical oxygen index (COI). LOI is the minimum concentration of oxygen, expressed as a volume percent, in a mixture of oxygen and nitrogen that will just support flaming combustion of a material under test conditions (ASTM D 2863). COI is the temperature in degrees Celsius at which the LOI of a material becomes 21 (the approximate percentage of oxygen in air) under test conditions (NES 715).

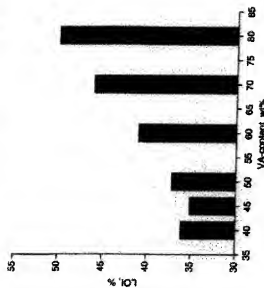
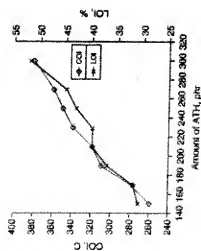


FIGURE 10.21 Influence of vinyl acetate content on limiting oxygen index. (EVM Compound with 190 phr aluminum trihydrate.)

As ATH withdraws energy from the flames by decomposing into aluminum oxide and water it has been found that increasing levels of ATH steeply raise the LOI and COI.

Figure 10.21 shows how the LOI is related to another factor, the vinyl acetate content of the EVM, which is varied when the filler content of the compound is held constant at 190 phr ATH.

At approximately 50% vinyl acetate, the increase of the LOI is disproportionately greater than that expected from linear reduction of the combustion enthalpy.

10.6.2.2 Toxicity, Smoke Density, and Corrosivity of Combustion Gases

All EVM polymers (VA-content 40%–80%) perform in a similar manner. Therefore, only the results of the EVM with 50% VA are exhibited in Table 10.9. The compound processes well with 190 phr aluminum trihydrate and provides low smoke density and low corrosion combustion gases.

10.6.2.3 Influence of Vinyl Acetate Content on Oil Swelling

With increasing vinyl acetate content, the polarity of the EVM becomes higher. Figure 10.22 shows the volume swell after immersion in ASTM oil No. 3 for 70 h at 150°C and dried fuel for 24 h at 70°C. The reduction in volume swell from 98% (40% VA) to 10% (80% VA) is noticeable. In addition, smoke and

TABLE 10.9

Flame Tests of a Typical FRNC Compound

Results of Flame Tests	
Toxicity Index, acc. NBS 713	1
Smoke density NBS chamber	
Acc. ASTM E 662-83	200
(W_{max} corrected) remaining smoke	166
(W_{max} corrected) flaming smoke	
Corrosivity of combustion gases	
Acc. NBS 318 Part 403	Pass
Acc. VDE 0472 Part 813	
Pb	3.8 (pass)
Conductivity, μ S/cm	52 (pass)

10.6.3 HEAT- AND OIL-RESISTANT MOULDED GOODS

An EVM with 60% vinyl acetate content is chosen as an interesting material for oil- and heat-resistant gaskets, oil seals, and other molded goods for service temperatures up to 150°C–170°C. Variation of vinyl acetate content will change the properties (swelling, low temperature flexibility) in the way already described. In spite of peroxide cure, the material does not require post curing to fully develop optimal physical properties.

Considering that the compounds were peroxide cured, the demolding and mold-filling characteristics in injection molding were surprisingly good. This has been proven by a plant trial using a Demam IM machine type 802 G using a two cavity mold for bellows. All tests were performed on samples press cured at 180°C for 10 min.

Table 10.10 shows the formulation of a typical compound for injection molding and accompanying properties.

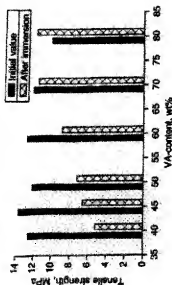
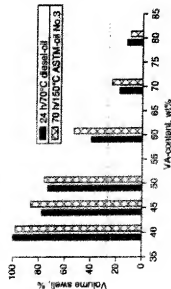


FIGURE 10.23 Influence of vinyl acetate content of EVM compound on tensile before and after aging in ASTM #3 Oil for 70 h at 150°C.

TABLE 10.10
EVM Injection Molding Compound

Injection Molding Compound	
EVM (60% VA)	100.0
N 550 carbon black	40.0
Stearic acid	1.0
Polyacrylonitrile stabilizer	3.0
Antioxidant 307A	2.0
Polyethylene wax	2.0
Zinc salt of fatty acid	2.0
TALC	1.5
Peroxide (40%)	5.0
Total	156.5
Physical properties	
Shore A at 23°C	62
Shore A at 70°C	50
Modulus at 100°C, MPa	3.2
Tensile, MPa	16.0
Elongation, %	380
Rebound, %	29
Tear, ASTM D 624 B, N/mm	22
Tear, ASTM D 624 C, N/mm	27
Die extrusion flow, cm ³	130
Raw materials	
Levapren KA 1335, Bayer	
Rhenogran P 50, Rhen Chemie	
Vulkatan TDA, Bayer	
Hoechstwax PE 520, Hoechst	
Alkaphat PP, Rheine Chemie	
Perkadox 301, AKZO	
Perkadox 14/40, AKZO	

TABLE 10.10 (Continued)
EVM Injection Molding Compound

Low-temperature properties	
Bottle point, °C	-46
TR 10, ASTM D 1329, °C	-23
TR 30, ASTM D 1329, °C	-15
TR 50, ASTM D 1329, °C	-13
Differential scanning calorimeter, 20°C/min, second heating cycle	
T _g , °C	-34
T _h , °C	29
Onset of glass transition process	
Glass transition temperature	
Aged in oil 14 days at 150°C-change	
Shore A, pts	6
Tensile, %	-4
Elongation, %	-15
Aged in ASTM #3 oil 72 h at 150°C-change	
Shore A, pts	-28
Tensile, %	-44
Elongation, %	-41
Volume, %	87
Aged in SAE 90 gear oil 72 h at 150°C-change	
Shore A, pts	-17
Tensile, %	-7
Elongation, %	-3
Volume, %	20
Aged in SAE 20W40 engine oil 7 days at 150°C-change	
Shore A, pts	22
Tensile, %	-19
Elongation, %	-26
Volume, %	37

10.6.4 EVM AS A BLEND COMPONENT

EVM is a soft copolymer and acts as a nonvolatile, nonextractable plasticizer, and processing aid when it is used as a blend component in compounds to improve processing by lowering the Mooney viscosity of the mix.

Two examples are given: first blend is based on chlorinated polyethylene (CM). By adding EVM to a light-colored CM compound the viscosity is reduced, as expected. The results are given in Table 10.11.

In addition, compression set and heat aging were improved without influencing tensile strength and elongation at break significantly.

The second example is a blend of EVM with a high vinyl acetate content and HNBR. As heat aging and oil resistance of both polymers are nearly identical both

compounds are suitable for blending. The two polymers show comparable over

TABLE 10.11
EVM/CM Blends in a Light-Colored Compound

EVM (DPA VA)	—	25.0	50.0	Leopren 500, Bayer
CM	100.0	75	50	Tyrim CM 0156, Dow
Ground CaCO ₃	60.0	60.0	60.0	Alumex, Polymer Valley Chemicals
Lead silicate	20.0	20.0	20.0	H-2021 D 80, Rhein Chemie
Spindolized aryl oil	10.0	10.0	10.0	Dynapex 6.8, Argus Chemical
Antioxidant SDBA	0.5	0.5	0.5	Valuonox DDA, Bayer
Coagulant	5.0	5.0	5.0	Stear 500, Sartomer
Peroxide	5.0	5.0	5.0	Perkadox 14/40, ARZO
Compound viscosity				
ML 1 + 4 at 100°C	74	64	41	
Physical properties, cured 15 min at 177°C				
Tensile, MPa	13.4	12.9	11.9	
Elongation, %	610	380	535	
Compression set B (ASTM D 395)				
70 h at 150°C, %	61	54	48	
Blend index (ASTM D 2137)				
Temperature, °C	-25	-30	-32.5	
Aged in air 70 h at 150°C-change				
Tensile, %	-55	-42	-39	
Elongation, %	-54	-30	-23	

Compared with an unblended HNBR compound additional benefits can be seen in the EVM/HNBR blend:

1. Lower price
2. Better heat aging
3. Better compression set at high temperatures, whereas oil swelling and cold flexibility are better with unblended HNBR

10.6.5 OUTLOOK FOR NEW APPLICATIONS

EVM elastomers have traditionally been used in the cable industry. But now some new applications are developed and EVM has been recognized as a heat- and oil-resistant material, which can be used for automotive applications, such as gaskets, seals, and hoses.

The demand for more safety in public buildings, subway stations, computer centers, and so on, has led to acceptance of the FRNC concept for flooring materials. Here EVM elastomers are tested as a basic component. Noise reduction for example, in workshops gave rise to another development: noise-densifying sheets and curtains. They are based on EVM elastomers filled with barium sulfate.

Lastly, EVM is a good blend polymer. In blends with polar polymers, such as CM,

TABLE 10.12
EVM/HNBR Blends in Black Filled Compound

EVM (90% VA)	—	25.0	50.0
HNBR (54% ACN)	100.0	75.0	50.0
ZnO	2.0	2.0	2.0
MgO	2.0	2.0	2.0
Acetic Acid SODA	1.0	1.0	1.0
Ammonium MMT	0.4	0.4	0.4
N 550-carbon black	45.0	45.0	45.0
TBAC	1.5	1.5	1.5
Peroxide	7.0	7.0	7.0
Total	158.9	158.9	158.9
Compression recovery			
ML 1 + 4 at 100°C	104	91	65
Physical properties			
Shore A, 90	72	75	76
Tensile, MPa	26.8	26.5	25.7
Elongation, %	325	290	210
Tear (DIN 53 515), N/mm	13.4	10.9	9.9
Compression set (DIN 53 515)			
70 h at 25°C, %	12	10	11
70 h at 150°C, %	27	24	22
Low-temperature properties			
T _g , DIN 53 546, °C	< -70	-68	-65
T _g , DIN 53 520, °C	-24	-25	-16
Aged in air 200 h at 150°C-change			
Tensile, %	-12	-4	-1
Elongation, %	-49	-34	-29
Aged in ASTM #3 Oil 72 h at 150°C-change			
Volume	25	31	32

As the need for specialty elastomers with good heat and oil resistance without halogen is increasing, expansion into other areas can be expected.

REFERENCES

- Perrin et al., GB 497643 App., JCI, 1938.
- G.W. Gilby, in *Developments in Rubber Technology*, Vol. 3, Eds. A. Whelan and K.S. Lee, Applied Science Publishers, New York, 1982, Chapter 4, "Ethylene-Vinyl Acetate Copolymers," pp. 101-144.
- W.D. Kenneth, Low Density Polyethylene (High Pressure)—Ethylene Polymers, Vol. 6, Ed. H.F. Mark et al., John Wiley & Sons, New York, 1966, pp. 360-429.
- R.D. Burkhart, N.L. Zurek, *Journal of Polymer Science Part A*, 1, 1137, 1963.
- H. Bartl, *Kautschuk Gummi Kunststoffe*, 452, 1972.

11 Polysulfide Elastomers

Stephen K. Flanders* and Robert C. Klingender

CONTENTS

11.1 Basic Properties of Solid Polysulfides.....	371
11.2 Compounding of Polysulfide.....	373
11.2.1 Vulcanization Agents.....	373
11.2.2 Plasticizing and Softening.....	374
11.2.3 Internal Lubricants.....	374
11.3 Fillers.....	375
11.4 Elastomer Blends.....	375
11.5 Processing.....	376
11.5.1 Thiokol FA.....	376
11.5.2 Thiokol ST.....	379
11.6 Applications.....	380
11.6.1 Paint Can Gasket.....	381
11.6.2 Paint Hose Inner Liner.....	382
11.7 Aum D2000 M, Type A, Class K, with Thiokol ST.....	383
11.8 Trouble Shooting.....	384
References.....	384

Polysulfides were first discovered and patented in about 1927 by J.C. Patrick by accident in attempting to develop an antifreeze. The polymer was called Thiokol A, a condensation reaction of ethylene dichloride and sodium tetrasulfide, for which manufacturing began in 1929 [1]. This elastomer was quite difficult to process due to its variability and thermoplastic nature, leading to the discontinuation of manufacture after improved grades were developed.

The current types of polysulfides are Thiokol FA, the workhorse for specialty rubbers, Thiokol ST designed for mechanical goods, and a series of liquid polymers, Thiokol LP, designed for sealants, coatings, and binders. Thiokol FA is an improved "A" type which uses approximately equal parts of ethylene dichloride and 1,1'-[methylene bis (oxy)] bis [2-chloroethane], or "formal." Polymerization takes place using a condensation reaction with sodium tetrasulfide for improved manufacturing control and processing, although the polymer is still very thermoplastic. Thiokol ST and LP are similar to each other in structure, except their molecular weights go from

* Stephen K. Flanders is deceased.